LASER SINTERING OF MATERIALS AND A THERMAL BARRIER FOR PROTECTING A SUBSTRATE

BACKGROUND OF THE INVENTION

This application claims the benefit of U.S. Provisional Application No. 60/198,377 filed April 19, 2000.

Several obstacles currently impede effective laser sintering of materials. One limitation is that current methods inhibit sintering throughout the material. A second problem is that adhesion of the material to a substrate is also inhibited.

Several factors exist that interfere with the propagation of sintering throughout a target material and with the adhesion of the target material to a substrate. A need exists for laser sintering of materials that overcomes these problems.

Existing laser sintering processes damage substrates that are not able to withstand the high temperatures associated with the laser sintering process. Substrates for directly written electronic circuitry are generally some type of plastic. Unfortunately, the highest temperatures known plastics can survive without degradation are on the order of 350 °C. Relatively few formulations can even survive at 200 °C. In contrast, most materials of utility in constructing electronics (e.g., metal conductors, metal or oxide resistors, and oxide dielectrics) melt at far higher temperatures. When such materials are to be formed into devices, their crystals or grains must have continuity with each other for electrical contact and with the substrate for adhesion. Continuity generally requires that individual particles be sintered into one conjoined

structure. In turn, the methods by which continuity may be achieved all require high temperatures approaching the melting point of the bulk material (T_m).

Therefore, the construction of high-T_m electronics components upon a low-T_m substrate presents a difficult materials-science challenge. A need also exists for protecting a substrate from laser damage during the laser sintering process.

SUMMARY OF THE INVENTION

The present invention is a method and apparatus for laser sintering of materials that provides complete sintering throughout the material and that enhances adhesion of the material to the substrate. Lasers may be used to sinter materials of interest to electronics applications.

The laser interacts with both the material to be sintered and the substrate upon which the material is positioned. This allows for a more complete heating process. The top of the material is heated via the laser and the bottom of the material is heated via the substrate. As the sintering occurs, the thermal spread throughout the material allows for sintering to occur completely through the material. This also enhances the adhesion significantly since the temperature difference between the substrate and the material are the same. If they are different, the temperature gradient stops the adhesion. This technique "fixes" both of the aforementioned limitations.

The present invention allows the laser to interact with both

the target material to be sintered and the substrate upon which it rests with controlled exposure times. This controlled dual interaction provides a more complete heating process. The top of the target material is heated by the laser, the bottom portion via the heated substrate. Diffusion of heat allows sintering to occur throughout the material. This controlled-dual-interaction procedure also significantly enhances adhesion because no temperature gradient exists between the substrate and the sintered material. Temperature gradients may interfere with adhesion. The laser-sintering technique of the present invention solves the aforementioned problems.

The present invention also includes a method and apparatus for protecting a substrate from laser damage during a laser sintering process. The present invention protects a low-T_m substrate with a thermal barrier coating designed to shield it from high temperatures. With such a thermal barrier in place, the electronics materials may be sintered into functioning components without damage to the substrate. This thermal barrier method works especially well with such deposition methods as laser-assisted chemical vapor deposition (LCVD) or laser sintering, in both of which laser irradiation provides a highly localized region of high temperatures.

A protective layer is placed on top of a low temperature substrate to provide a protective thermal barrier. The thermal barrier allows for exposure to much more intense laser irradiation, thereby aiding in the sintering of deposited

materials. The thermal barrier may be applied to any material. Several benefits are provided by the use of a thermal barrier on a substrate during a laser sintering process. One benefit is that the substrate is protected from the excessive heat of the laser sintering process. A second benefit is that adhesion of the deposited material to the substrate is enhanced.

These and further and other objects and features of the invention are apparent in the disclosure, which includes the above and ongoing written specification, with the claims and the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-section of a line of silver paste that has been sintered.

Figure 2 is a top view of a line of silver paste that has been sintered.

Figure 3 is a graph of laser pulse duration vs. laser penetration depth into a material.

Figure 4 is a diagram of an alumina substrate with parallel silver tabs that are perpendicular to the laser scanning direction.

Figures 5A and 5B are plots of laser voltage and temperature vs. time for open and closed loop feedback.

Figure 6 is a perspective view of a laser sintering apparatus that is controllable through a CAD/CAM interface.

Figure 7 is a diagram of a simulation geometry of a stack-up

of silicon, aerogel, and silver to be sintered by a laser process.

Figure 8 is a graph of power density vs. pulsing time showing the maximum silver temperature with a 1 μm layer of aerogel.

Figure 9 is a graph of the power required to raise a silver layer to its melting point as a function of pulse time and power intensity.

Figure 10 is a graph of the power required to raise a silver layer to its melting point and a silicon substrate to 400 K with a 1 μm aerogel layer as a function of pulse time and power intensity.

Figure 11 is a graph of the power required to raise a silver layer to its melting point and a silicon substrate to 400 K with a 10 μm aerogel layer as a function of pulse time and power intensity.

Figures 12A and 12B are perspective views of silver line laser-sintered onto a plastic substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The laser processing of materials involves consideration of several aspects of the target material. First, the laser-power density (Φ) needed to accomplish laser sintering is strongly dependent upon the light-absorption characteristics of the material, chiefly absorptivity (α), which is in turn dependent upon temperature (T), light wavelength (λ), and light temporal

pulse width or duration (τ). Materials are used for which the sintering temperatures (T_s) are much lower than their bulk melting points (T_m). However, the present invention provides a method of laser sintering of any material without damaging the substrates upon which they rest. Typical values for some materials of interest are listed in Table I.

The effects of low α at a particular λ have significant consequences. The initial material dispensed is composed of various compounds and solvents, all of which change the absorption behavior of the composite. The initial composite is "wet" and must be treated appropriately. If not, the laser may "splatter" the paste and destroy the device. A drying process must be used to reduce the solvent concentration; however, even small amounts of remaining solvent often strongly absorb the laser.

The interaction of the laser light and matter causes the sintering process to begin. In the example shown in Figure 1, a continuous-wave (CW) CO_2 laser (λ = 10.6 μm) was used to sinter silver paste 1. It should be noted that the only portion actually sintered is a thin layer 3 at the top of the material 1. Once the top few layers of the material 1 are sintered, they form a highly reflective mirror at λ = 10.6 μm, which diverts the laser energy and prevents sintering from occurring throughout the deposit.

With a laser, it is possible to inject a tremendous amount of energy, which translates to heat, into a material. Once the

absorption behavior is known (more is better), then the effects of pulse duration (τ) must be determined. Peak powers (P_{max}) in the gigawatt range are obtainable using lasers with low energy per pulse but very short pulses. Tradeoffs must be made to optimize τ. Shorter τ yields higher P_{max} but this works adversely with penetration depth (δ) in that shorter τ yields shorter δ. Therefore, if τ is too short, the interaction is confined to the surface 5 of the target material 7, as occurred with the sample shown in Figure 2. In that case, a silver paste 7 sintered with a pulsed laser, a XeCl excimer (λ = 308 nm), the top 5 of the paste deposit 7 was sintered but not the bottom or middle. The fact that a very thin layer was sintered demonstrates that a strong interaction exists between the silver and the 308-nm laser; however, τ was too short for deep and complete penetration.

If τ 9 is extended out to infinity ($\tau = \infty$), i.e., CW mode, then the interaction area extends completely through the paste, into the substrate, and even through the substrate. Therefore, it should be possible to control δ 11 (penetration depth plotted on the vertical axis) by controlling τ 9 (pulse duration plotted on the horizontal axis), as illustrated in Figure 3. As is shown on the curve 13, as the pulse duration lengthens, the penetration depth becomes larger. Note that the penetration depth increases as you move down the vertical axis.

The propagation behavior of the thermal wave throughout the sample material was verified with a thermal-imaging camera. The

longer the pulse, the farther the thermal wave traveled. Controlling τ enables δ to be made the same as the thickness of the material (θ). Several nontrivial factors must be considered when implementing this into a CAD/CAM program. They must even be considered in a laboratory setting if reproducibility is a requirement. The best way to ensure reproducibility is through a feedback control system. Such a system has been implemented by using a pyrometer with a relatively small (25 μm) spot size. While many pyrometers are available in the market today, the combination of small spot size and low temperature range is unique.

The output of the pyrometer was sent to the same computer that controls the output of the laser. The effectiveness of this method was demonstrated by setting the laser power to a constant value, then scanning it across a substrate 15 containing metal lines 17 parallel to each other and perpendicular to the laser scanning direction, as shown in Figure 4. The output of this experiment showed dramatic differences and verified the effectiveness of active thermal feedback in controlling the power of the laser. Figures 5A and 5B show the results of open and closed loop feedbacks, respectively.

The present invention also includes a machine tool that implements the materials and the laser processes. The present invention allows its end user to interface to CAD/CAM, allowing for a fully automated machine needing very little interaction with or expertise by the user. The apparatus is capable of

depositing and processing the desired materials over "any" surface with resolutions as small as 10 μm.

The present invention is capable of depositing lines as small as 75 μm. With the right paste, the shape of the line may be held. The apparatus may write on flat, slightly angled, or dipped surfaces. Preferably, the apparatus has a vertical travel of approximately 1 mm with good precision. In another embodiment, the apparatus is capable of writing over much larger vertical changes.

Figure 6 is a perspective view of a preferred embodiment of the apparatus 19 of the present invention. The apparatus includes a drying process and two lasers found necessary to cut, drill, and sinter all of the electronics materials, which have large variations in light-absorption behavior. Preferably, the two lasers used are a CO_2 laser and a diode-pumped $Nd:YVO_4$ laser. As noted previously, the CO_2 laser emits radiation of $\lambda = 10.6$ μm, which is relatively long and is conveniently absorbed by many materials. The $Nd:YVO_4$ laser emits near-infrared radiation at $\lambda = 1.06$ μm; while the base wavelength is not optimal, it may be frequency-upconverted via nonlinear optics into ultraviolet radiation of $\lambda(3\nu) = 355$ nm or $\lambda(4\nu) = 266$ nm to reach desired absorption windows. The apparatus also includes a computer so that a user may interface with CAD/CAM software, allowing for a fully automated machine needing very little interaction with or expertise by the user.

The present invention also provides a protective layer that

is placed on top of a low temperature substrate to provide a protective thermal barrier. The thermal barrier allows for exposure to much more intense laser irradiation, thereby aiding in the sintering of deposited materials. The thermal barrier may be applied to any material. Several benefits are provided by the use of a thermal barrier on a substrate during a laser sintering process. One benefit is that the substrate is protected from the excessive heat of the laser sintering process. A second benefit is that adhesion of the deposited material to the substrate is enhanced.

One preferred thermal barrier material is an aerogel. An aerogel coating was placed onto some typical low-T_m circuit board laminate samples. A simple device was constructed and laser-sintered on thermal-barrier-coated and uncoated substrates. The coated substrate suffered significantly less damage than did the uncoated substrate.

A series of one-dimensional rapid thermal processing (RTP) simulations were performed for the geometry shown in Figure 7 using the data listed in Table II. The purpose of these simulations was to investigate the potential benefits of aerogel as an insulator and to develop an approach for characterizing multilayer processing.

In the simulations, a stack-up 113 of a silicon substrate 101, an aerogel thermal barrier 103, and a silver deposition material 105 was pulsed once with a uniform distribution of power density (in W/m^2) 107. The intensity and duration of the pulse

was varied. The sides 109 and bottom 111 of the stack 113 are assumed adiabatic. As such, all the energy of the pulse remains in the stack 113. The results of interest are the maximum temperatures that occur in each layer as a function of pulse length and intensity.

Figure 8 shows the maximum silver temperature as a function of the pulsing time and power density for the configuration with a 1-μm layer of aerogel. The total energy per unit area (E_{in}) deposited into the stack is the product of the pulse duration (τ) and power density (Φ). At a low E_{in}, the temperature of the silver remains near the initial temperature T_0 = 300 K. At a higher E_{in}, the temperature of the silver exceeds T_m = 1235 K. In between these two extremes, the maximum silver temperature ranges between 300 K and T_m. The isotherms depend not only on the total energy but also on the combination of pulse and intensity used to input that energy. Note that temperatures computed as above T_m were reset to 1235 K.

When the energy was added in a short burst, it was fully absorbed by the top layer of silver 105 before it had time to diffuse through the aerogel 103 into the substrate 101. Conversely, adding the same energy over an extended period allowed the energy time to conduct to the substrate 101, thus evenly heating all layers 101, 103 and 105. The bounding, straight lines 115 and 117 on Figure 9 correspond to these two extremes. The lower bound 115 is the E_{in} needed to heat the silver to T_m if all the energy went into the silver. The upper

bound 117 is the E_{in} that would be required to melt the silver if that energy were distributed to all layers. As expected, more energy is required to melt the silver if some of the energy is distributed to other materials.

In between these two bounds 115 and 117, the actual energy required to bring the silver to melting depends on the combination of pulse duration and intensity used. Furthermore, the transition from one limit to the other depends on the thickness of the insulating layer 103 between the substrate 101 and the silver 105. Figures 10 and 11 show the computed energy required to obtain the silver melting point as a function of intensity and pulse duration for two different geometries, aerogel layers of 1 and 10 μm.

The combination of pulse duration and intensity used to bring the silver to its melting point becomes critical when the peak temperatures of other layers are of concern. For example, Figure 10 includes a plot of the combinations of duration and intensity required to heat the silicon substrate to 400 K for the stack-up with a 1-μm thickness of aerogel, represented by curve 121. When this curve 121 is compared with the corresponding melting-point curve 123 for silver, the conclusion is that no combination of pulse duration and intensity can satisfy the dual requirement that the silver be heated to 1235 K while the silicon substrate be maintained at or below 400 K. However, this condition is met if the thickness of the aerogel is increased to 10 μm, as indicated by the overlapping curves 125 and 127 at

point 129 in Figure 11.

After an aerogel layer put on a substrate to protect its surface was tested in simulation, the aerogel layer was then tested on simple electronic components. In a trial study illustrated in Figures 12A and 12B, the component was a silver conductor line. The aerogel-silver composite was observed to interact strongly with a laser (any laser). If the component placed on top of the aerogel protector is too thin, the laser will damage the aerogel layer, but not the substrate. If the laser interacts only with the component and not the aerogel, the presence of the aerogel layer becomes a significant advantage. As shown in Figures 12A and 12B, a laser-sintering test run on a silver conductor with and without an aerogel layer, holding the laser power constant on both samples, produced readily apparent differences in results. The unprotected substrate shows considerable damage; the aerogel-protected one does not.

While the invention has been described with reference to specific embodiments, modifications and variations of the invention may be constructed without departing from the scope of the invention, which is defined in the following claims.